Overall Crystallization Kinetics; Equation of Kolmogorov, Johnson, Mehl, Avrami

Overall crystallization of a melt is a complex process involving simultaneous nucleation and growth of separate crystallites. It was first described by **K**olmogorov in 1937, **J**ohnson and **M**ehl 1939; **A**vrami 1939,1940,1941.

KJMA THEORY

General formulae

The main quantity to be determined in the theory of overall crystallization is the total volume V_c of crystalline phase, or equivalently, the fraction $\alpha \equiv \frac{V_c}{V_o}$ of volume crystallized till time t. In KJMA theory it is assumed that V_c results from nucleation of material points at a rate $J(t)$ ($m^{-3}s^{-1}$) which then only expand in radial direction with growth rate $G(t)$ (m/s)

At initial moments there are no contacts between the growing crystals. For that reason, at time t the volume $V_n(t',t)$ of any individual *n-sized* crystallite depends only on the earlier moment $t' £ t$ of its nucleation provided it is additionally assumed that the crystallites are isomorphic during growth. The so-called ***extended volume*** V_{ex} is given by:

$$V_{ex}(t) = w\int_0^t \mathrm{V_o}\, J(t')\left(\int_{t'}^{t} \mathrm{G}_n(t',t)\,\mathrm{dt''}\right)^n dt' \qquad (1)$$

V_{ex} is the whole crystalline volume that would have formed in the melt till time t if there were no exhaustion of the initial melt volume. To know V_c during the entire process we must extend the validity of the above equation beyond the initial stage, so that the process can take place only in the non crystalline volume V_o-V_c

$$\alpha_{\mathrm{ext}} = \frac{\mathrm{V_{ext}}}{\mathrm{V_o}}$$

Avrami has shown then:

$$\mathrm{d}\alpha(\mathrm{t}) = (1-\alpha)\,\mathrm{d}\alpha_{\mathrm{ext}} \qquad (2)$$

$$a(t) = 1 - \exp[-a_{ex}(t)] \qquad (3)$$

Since the crystals are assumed to keep their shape during growth, geometrically, at time *t* a given crystallite can be characterized by an effective radius *R* which depends on the earlier moment *t'* of its formation.

$$V_n(t',t) = c_g R^d = c_g \left[\int_{t'}^{t} \mathrm{G}(t'')dt'' \right]^d$$

Here c_g (m^{3-d}) is a shape factor.

Finally

$$a(t) = 1 - \exp\left\{ -c_g \int_0^t J(t') \left[\int_{t'}^{t} \mathrm{G}(t'')dt'' \right]^d dt' \right\}$$

This is the evolution of the crystallized fraction of the volume. It is controlled by two basic parameters – the crystallite nucleation and growth rates *J and G*

For *G=const , and J=const*

$$\boxed{a(\mathrm{t}) = 1 - \exp\left(\frac{\mathrm{c_g}}{\mathrm{d}+1} \mathrm{JG^d t^{d+1}} \right)}$$

The time t_x for which a given degree of crystallinity *x* is reached is:

$$\mathrm{t_x} = \left(-\frac{(\mathrm{d}+1)\ln(1-\mathrm{x})}{\mathrm{c_g JG^d}} \right)^{\frac{1}{\mathrm{d}+1}}$$

Growth	*Shape*	c_U
1D	*Needle*	$2A_o$
2D	*Disk*	pH_o
2D	*Square prism*	$4H_o$
3D	*Sphere*	$4p/3$
3D	*cube*	*8*

A_o – constant cross section area of needle; H_o constant thickness of the prism

According to Kolmogorov α(t) can be interpreted as the probability for crystallizing the melt until time *t* after the onset of the process. This means that the average time t_{av} for crystallizing the melt is:

$$t_{av} = \int_0^\infty t\,da(t) = \int_0^\infty exp\left[-\frac{V_{ex}(t)}{V}\right]dt$$

Knowing *a(t)* we can determine the number *N(t)* of crystallites at time

$$N(t) = V_o \int_0^t J(t')[1-a(t')]dt' = V_o \int_0^t J(t')\exp\left[-\frac{V_{ex}(t')}{V}\right]dt'$$

With *N(t)* the average volume V_{av} of crystallites at the end of overall crystallization is:

$$V_{av} = \frac{V_o}{N(t)} = \frac{1}{\int_0^\infty J(t)\exp\left[-\frac{V_{ex}(t)}{V}\right]dt}$$

Derivation of Kolmogorov

Assume that $P(t) = \frac{V_c(t)}{V}$ is the probability that a given point is crystalline. The probability that a new crystalline nucleus will be formed in amorphous part *V'£V-*V_c during time *Dt is* P_i*=JV'Dt*.

Large volume – i.e. we discuss points at a distance larger than G*Dt* from the surface of the sample

At time *t* an arbitrary chosen point will be inside a crystal if at time $t_i < t$ in some other point at a distance $r < G(t-t_i)$

a new crystal appears. The volume $V'(t_i)$ inside which is this point is:

$$V'(t_i) = K(n) r_{max}^n = K(n) G^n (t - t_i)^n$$

For sphere $K(n)=4p/3;\ n=3$

The probability P_i that a nucleus is formed during time Dt in volume V' is

$$P_i = JV'(t_i) Dt_i = K(n) J G^n (t - t_i)^n Dt$$

Remember: Always the reverse probability – the event will not happen is important! $q_i = 1 - P_i$

<u>*Let*</u> time t is separated to s intervals $t = sDt$

$$q(t) = \prod_{i=1}^{s} q_i = \prod_{i=1}^{s} (1 - P_i) \quad ; where \ \ t_i = iDt$$

For short Dt *the probability* P_i *is* <u>*small*</u>, therefore:

$$q(t) = \prod_{i=1}^{s} (1 - P_i) = \prod_{i=1}^{s} e^{-P_i}$$

$$\ln q = -\sum P_i = K(n) G^n \sum (t_i - t)^n Dt$$

Under the transition to infinitesimal time intervals $Dt \to dt$

$$\ln q(t) = K_n \int_0^t G^n J (t - t)^n dt = -\frac{K_n}{n-1} G^n J t^{n+1}$$

or

$$a = 1 - \exp\left[-\frac{K_n}{n-1} G^n J t^{n+1} \right]$$

In the case of athermal nucleation the power n is reduced by 1 and instead J appears the number of athermal nuclei per unit volume.

The rate of overall crystallization is:

$$W(t) = \frac{da(t)}{dt} = K_n G^n J t^n [1 - a]$$

If relatively small grains are crystallizing from the surface the problem is solved by Todes.

Non steady state effects:

$$a(t) = 1 - \exp\left\{ -c_g \int_0^t J(t') \left[\int_0^{t-t'} G(t'')dt'' \right]^d dt' \right\}$$ the time dependence of *J* ***must be taken into account***

Simplest approximation:

$$J(t) = \begin{cases} 0, & for\ t < t \\ J & for\ t > t \end{cases}$$

In this case the time necessary to reach a given degree of crystallinity is: $\bar{t}_a^* = \bar{t}_a + t$

The Avrami equation reads:

$$a = 1 - \exp\left(-Kt^n\right) = 1 - \exp\left(-\left(\frac{t}{t}\right)^n\right)$$

$$K = \pi G^m J$$

Correspondingly, the characteristic time of the process is:

$$t = \frac{1}{(pJ)^{\frac{1}{n}} G}$$

The results on overall crystallization kinetics are, usually, analyzed in coordinates *ln (-ln (1-a))* against *ln t.* However, the double logarithmic function exaggerates experimental errors in the limiting cases: both at $\alpha \to 0$ as well as at $\alpha \to 1$.

New Coordinates *a vs ln t*. An *S-shaped* curve, varying between 0 and 1, appears.

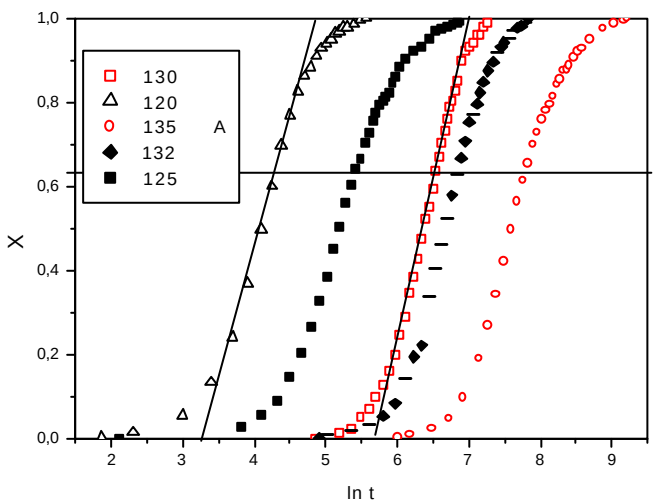
$$\frac{\partial a}{\partial \ln t} = n\left(\frac{t}{\tau}\right)^n e^{-\left(\frac{t}{\tau}\right)^n}$$

$$\frac{\partial^2 a}{\partial (\ln t)^2} = \left(1-\left(\frac{t}{\tau}\right)^n\right) n t^n e^{-\left(\frac{t}{\tau}\right)^n}$$

It is seen that the curve has an extremum at $t=\tau$, *resp.* $a=1-1/e=0.63$.

The slope at this point is $a'(t=\tau)=\frac{n}{e}=0.368n$. This slope intercepts abscissa at an onset point $\ln t_1$. The intercept with $\alpha=1$ gives the end point of the process at $\ln t_2$. The parameter n is easily determined by the difference

$$\ln t_2 - \ln t_1 = \frac{e}{n}$$



$$a = 1 - \exp\left[-cJt(Gt)^{d}\right]$$

N=Jt **Gt® Gt$^{1/2}$**

d	N		J	
	t	$\sqrt{t}$	t	$\sqrt{t}$
one	1	1/2	2	3/2
two	2	1	3	2
three	3	3/2	4	5/2

OSTWALD RIPENING

The Ostwald ripening process is best described by the Lifshits-Slyozov-Wagner model. It follows from the Thompson-Gibbs equation according to which solubility depends on the size of crystal r as:

$$C = C_{\infty} \exp\left(\frac{2\sigma V_m}{kTr}\right)$$

This gives a thermodynamic driving force for transport of material from small crystals to large ones. If the diffusion is the slowest process than the size of the average radius <*r*> has the following time evolution:

$$\left(\frac{<r>}{r_{in}}\right)^3 = Kt \qquad (1)$$

Here K accounts for the diffusion coefficient.

In order to have the size distribution function in an appropriate form it is useful to introduce the dimensionless size $\rho = \frac{r}{<r>}$. The size distribution function has the form:

$$f(\rho) = \rho\left(\frac{3}{3+\rho}\right)^{\frac{7}{3}}\left(\frac{1.5}{1.5-\rho}\right)^{\frac{11}{3}} \exp\left(\frac{\rho}{1.5-\rho}\right), \ \rho<2/3 \qquad (2)$$

According to the same model, in the case when rate determining is the kinetics of the reaction at the interface (dissolution/incorporation) the two equations are:

$$\left(\frac{<r>}{r_{in}}\right)^2 = Kt \qquad (3)$$

and

$$f(\rho) = \rho\left(\frac{2}{2-\rho}\right)^5 \exp\left(\frac{3\rho}{2-\rho}\right), \ \rho<2 \qquad (4)$$

In order to compare the theory and experimental data, the latter must be renormalized to one. For this reason the number of each class of the histogram should be divided to the overall number of

crystals. The distribution curve could be also described by Gaussion distribution.

The model can take into account additional complications like the influence of the volume of the ripening phase or the coalescence of particles.

From Eqs.(1,3) one can determine K and plot it in Arrhenius coordinates (if data at different temperatures are available) to determine the activation energy.